

Time-Domain Curve Fitting for Automated Oil Core NMR Spectral Analysis

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ABSTRACT

Automated analysis of nuclear magnetic resonance (NMR) spectra is critical for accurate quantification of oil and water in cores: ultimately, one can expect to process hundreds of samples per day. In the NMR experiment, several data points at the beginning of the NMR signal are missing because of radiofrequency (RF) pulse breakthrough or electrical ring-down of the receiving coil. A Fourier transform of the incomplete data produces a distorted spectrum. Also, quantification depends on knowledge of the signal amplitude at time zero, and the rapid decay of the NMR signal in some rocks can lead to inaccuracies.

For water and oil in rocks, the number of spectral components is small. Therefore we have taken the approach of fitting a small number of functions to the time-domain data to find the global minimum of the chi-square difference between theory and data. The minimization (using a commercial mathematical routine) generally takes a few minutes and results in values for the amplitudes and decay constants of the time-domain signals corresponding to the various spectral components. Time-domain fitting allows back projection to time zero of signals that are attenuated by decay (e.g. water and oil in shaly sandstones).

INTRODUCTION

Oil core nuclear magnetic resonance (NMR) imaging/spectroscopy is presently a research activity, and images and spectra can be examined and analyzed individually. In the long run, however, the examination of hundreds or

thousands of feet of core will require automated analysis to make sense of the resulting enormous amount of data.

The simplest NMR spectroscopy experiment consists of acquiring NMR data (the "free induction decay" or FID) following an applied radiofrequency (RF) pulse. The first few data points of the FID are usually corrupted by interference from the applied RF pulse which typically takes tens or hundreds of microseconds to decay to a low enough level so that real NMR data can be acquired. The Fourier transform (FT) is generally used to convert the time-domain FID to a spectrum. However, when applied to the incomplete FID, the FT gives distorted spectra which include undesirable baseline roll which makes quantitation of the various spectral lines difficult. This is known as the "missing points" problem. Various corrections are then manually applied by the spectrometer operator to flatten the baseline.

A number of spectral estimation methods have been developed to cope with the missing points problem in the time domain, the most successful and quantitative being the "linear prediction" (LP) technique (e.g. Barkhuijsen *et al* 1985). However, the LP technique works only with Lorentzian lineshapes, that is, signals that decay exponentially. LP does not work with Gaussian lineshapes, whose time domain function is also Gaussian, or with the carbonate powder pattern (Mehring, 1982), which we will discuss later. Fortunately, oil and water in rocks generally produce only two or three spectral lines, contrasted with a very large number of spectral lines in analytical NMR and 10–15 lines in *in vivo* spectroscopy. So in the oil core case, simple fitting procedures can converge in reasonable time.

We present the following examples: ^1H spectroscopy with an oil line and a water line; ^{13}C spectroscopy with an aliphatic spectral line and an aromatic line; and a carbonate powder pattern.

METHOD AND MATERIALS

NMR system

Data was take using GE 2T, 31 cm horizontal bore NMR systems (at Shell BRC, Houston and GE CRD, Schenectady) with 3" and 4.5" ID RF coils.(Hayes *et*

al 1985,Edelstein et al, 1988)

Computer and software

All the curve fitting was performed on a Data General MV10000 minicomputer (hereafter abbreviated as MV10). The MV10 operates at 3 MIPs, which is a moderate speed by today's standards, and therefore the processing time will decrease as the application is moved to modern workstations.

The programs were all written in FORTRAN 77. The chi-square of the difference between the theoretical free induction decay (FID: sums of decaying Lorentzians or Gaussians and/or carbon powder pattern) and the time-domain experimental data was formed and minimized using the commercially available subroutine ZXMWd from IMSL (IMSL). ZXMWd is described as "Global minimum (with constraints) of a function of N variables."(IMSL) The important inputs to ZXMWd are the function to be minimized (in this case the chi-square), a range of values for each parameter searched specified by an array, and a number of starting points. ZXMWd then searches phase space within the constraints set by the input arrays. The parameters in our fit include the amplitude of each line, the frequency, the decay time and the phase.

As mentioned above, some of the initial points in the FID have to be thrown away because they are contaminated by RF pulse breakthrough from the transmitter. It is also true in some cases that the initial part of the data contains fast-decaying NMR signal which may come from materials composing the RF coil or sample holder. Using only the data that comes after the fast-decaying signal can eliminate spurious results from that signal. If sufficient signal-to-noise ratio (SNR) still remains after getting rid of the first few points, then the time-domain fitting technique will work well. In contrast, eliminating initial points from the FID commonly produces distorted baselines in the Fourier transformed (FT) signal which are commonly dealt with by slow, operator-intensive and somewhat subjective manipulation of the resultant spectrum. So the FT is certainly not the best way to examine the spectrum of a signal which is missing a substantial number of initial points.

Curves used in fitting.

Three curves were used in fitting the spectra of interest. These are Lorentzians, Gaussians and powder patterns.

The Lorentzian line is a result of an exponentially decaying, sinusoidally varying time-domain signal and is the theoretical lineshape for a pure NMR species in a homogeneous magnetic field. Its time domain form is given by

$$S(t) = \exp(j\omega_0 t - t/T_2 + j\phi) \quad (1)$$

where ω_0 is the center frequency, T_2 is the signal decay time and ϕ is an arbitrary phase. The real part of the corresponding frequency domain spectrum is

$$S(\omega) = \frac{1/T_2}{(\omega - \omega_0)^2 + \frac{1}{T_2^2}} \quad (2)$$

The time-domain signal and spectrum of the Lorentzian are shown in Figure 1.

The Gaussian time domain function is given by

$$S(t) = \exp(j\omega_0 t - t^2/(2T_2^2) + j\phi) \quad (3)$$

where this time the signal decay is of Gaussian form. The Fourier transform of a Gaussian is a Gaussian. However, the exact form of the spectrum in terms of the Gaussian time domain function involves error functions and we will not detail it here. Figure 2 shows the time domain Gaussian function and its spectrum as obtained by Fourier transform. Gaussian lineshapes occur in our case when we have a whole collection of overlapping lines (^{13}C NMR).

Comparing Figs. 1(a) and 2(a), it is apparent that the Lorentzian envelope slopes down from time zero while the Gaussian envelope is flat at time zero. The spectral forms of Lorentzian and Gaussian lineshapes (Figs. 1(b) and 2(b)) differ in that Lorentzian lines have wider wings. So the first step in curve fitting in either the time or frequency domain is to determine, by inspection and knowledge of the physics, which lineshape is appropriate.

The symmetric powder pattern (Mehring, 1982; Vinegar et al, 1989), which applies to ^{13}C spectra of the C in carbonates, is a broad, hyperbolic spectral distribution $S(\omega) \sim 1/(\omega - \omega_0)^{1/2}$ where ω extends from ω_0 to some ω_{max} . In practice, the powder distribution is broadened by the time domain signal decay so that the infinity at $\omega = \omega_0$ does not occur. To adapt the powder pattern to digital form we take the spectral powder distribution to be $S(k) \sim 1/(k - k_0)^{1/2}$ with integer k going

from k_0+1 to some k_{max} . At $k=k_0$, we set $S(k) = 2$. A time-domain powder function is produced by numerically transforming back to the time domain and multiplying by a decaying exponential or Gaussian apodization. A broadened powder pattern can be produced by transforming back into the frequency domain, and several examples of broadened powder patterns (Vinegar et al, 1989) are shown in Fig.3.

OIL/WATER PROTON SPECTRA IN CORE PLUGS

Time-domain fitting was applied to the core plug data described in Table 3 of Edelstein *et al*, 1988 and associated text. This data came from an experiment in which water in one-inch core plugs was displaced by Soltrol-130 oil centrifuged into the plugs. The oil saturation (S_o) in the plugs was determined by mass balance and centrifuge production and compared to S_o determined by NMR. In (Edelstein *et al*, 1988), the NMR quantification was done using the following steps: 1) Data acquisition; 2) subtraction of background spectrum; 3) Fourier transform; 4) apply corrections to eliminate baseline distortion; 5) fit Lorentzian lines to the NMR spectrum. This process requires substantial operator interaction and takes about 5 minutes for each spectrum.

Examination of the time domain data indicated that the two spectral lines to be fitted should be Lorentzian. This makes sense because the theoretical lineshape of a single NMR line should be Lorentzian, although other circumstances (such as inhomogeneous magnetic fields) may tend to make the lines more Gaussian.

Fig.4(a) shows the uncorrected proton spectrum for water and Soltrol-130 in Bentheim (see Bentheim sandstone, second pass in Table 1 below). Fig 4(b) shows the spectrum following background correction applied to 4(a). Figure 5(a) shows the time-domain FID for the above along with a time-domain fit. Note the kink at the beginning of the measured data. This is probably short-lived signal from the sample holder and accounts for the broad baseline hump in Fig. 4(a). The initial few points of the FID have been discarded before fitting, thereby avoiding the problem of dealing with the spurious NMR signal from the sample holder. Fig 5(b) is the spectrum corresponding to data shown in Fig. 5(a). The solid line is the FT of the measured data with initial several points supplied from theoretical

data and the dashed line is the FT of the fitted function.

Table 1 shows the results of the fittings, which took an average of 78 seconds. In general, the TD (time-domain) determination is similar to the FD (Fourier domain) result and S_0 as determined by MB (mass balance). The results for the third pass for Bentheim was a problem since there was essentially one peak (with a possible bump on the side) which turned out to be difficult to analyze with either time-domain fitting or FD fitting; basically, it looks like a single peak, with a slight bump on the side.

Table 1.

Soltrol-130 oil saturation measurements in one inch plugs

Sample	Centrifuge pass	TD Oil frac.	FD oil frac.	MB oil frac.	CP oil frac.	Fitting time (s)
Indiana limestone	First	0.20	0.18	0.18		84
	Second	0.29	0.28	0.27		57
Bentheim sandstone	First	0.19	0.22	0.24	0.24	74
	Second	0.50	0.46	0.47	0.50	64
	Third	1.00	0.96	0.91		115
Bakers dolomite	First	0.22	0.21	0.26	0.20	101
	Second	0.37	0.46	0.43	0.41	48
	Third	0.68	0.65	0.64		82

Notes: "TD" means "time domain", "FD" means "Fourier domain"; "MB" means "mass balance; "CP" means "centrifuge production".

¹³C SPECTRA IN WHOLE CORES

¹³C NMR spectra of whole core appears to be a promising method of determining bulk volume of movable oil, aliphatic/aromatic ratio, oil viscosity and organic vs. carbonate quantity (Vinegar et al, 1989), particularly in cores such as Berea sandstone with substantial shale content where linewidths are broad and the ¹H water and oil peaks overlap. For oil in cores, the aliphatic and aromatic ¹³C peaks are centered at about -30 ppm and -130 ppm respectively which leaves them clearly separated by about 100 ppm with FWHM about 30 ppm. These broad peaks consist of a large number of unresolved, overlapping peaks, and the result appears to have a Gaussian shape, which is the form that we use for fitting in this case. The other important contribution to the ¹³C spectrum is the carbonate powder pattern (whose form is described above), which extends from about -200 ppm to -120 ppm. Therefore the aromatic oil ¹³C peak falls on top of the 120 ppm end of the powder pattern(Vinegar et al, 1989).

Fitting oil spectra in sandstones.

Bentheim and Berea sandstones contain no carbonate so the spectrum of oil in these rocks consists only of aliphatic and aromatic resonances. In this case we used 5 1/4" ID RF coils to examine completely oil-saturated Bentheim and Berea whole cores approximately 2" diameter by 2" long (Vinegar *et al* 1989). Approximately 150 μ s of initial data was discarded because of large spurious initial signal from transmitter breakthrough or RF coil ring-down. (Lower RF frequencies tend to increase ring-down time). A width of 30 ppm as mentioned above (corresponding to 645 Hz) and the separation of the two peaks by 100 ppm (corresponding to 2150 Hz) means that initially the signal is dropping rapidly. So Fourier transforming without the initial 150 μ s of data may produce spectral distortion. Time-domain fitting should, in principle, be able to project the signal back to time zero and obtain the correct oil saturation.

Figure 6 shows (a) measured data and Gaussian fit to the time-domain signal of Wasson crude in Bentheim and (b) the theoretical spectrum and spectrum derived from the measured data by filling in missing initial data points from the theoretical fit. Figure 7 is the same for Berea sandstone containing

Wasson crude. The fits for Bentheim and Berea took 60 s and 55 s respectively.

Using the MB determination of oil saturation in the Bentheim core as a standard, the fitted function gave a crude oil weight of 17.6 g for Berea using the Berea/Bentheim aliphatic amplitude ratios only and 16.7 g using Berea/Bentheim aliphatic + aromatic ratios. The Berea oil weight determined by mass balance was 20.8 g. The hand-processed FD spectra gave only 13.8 g. The fitted values are higher and closer to the actual weight than the hand-processed values, which may be related to the ability of the TD fitting method to extrapolate to time zero. However, there is apparently still some missing oil, which may be attributable to a short relaxation time component that neither method is seeing.

Fitting carbonate powder spectra

Figures 8a) and 8b) show, respectively, a time-domain carbonate signal and spectrum along with an excellent theoretical fit. In this case the fit took about 5 minutes.

SUMMARY AND CONCLUSIONS

Automatic processing of spectra is essential for oil core NMR analysis/imaging. Since proton and carbon spectra of water and oil in rocks tend to be simple (a few peaks), a direct approach of fitting the free induction decay in the time domain using a computer search to minimize chi-square seems to be suitable. The ability of time-domain fitting to project back to time zero after loss of initial data points may prove important in accurate quantitation of oil and water saturation.

Future plans for this work include fitting powder spectra and oil peaks simultaneously for ^{13}C spectra and configuring the software to pipeline a large series of spectra automatically.

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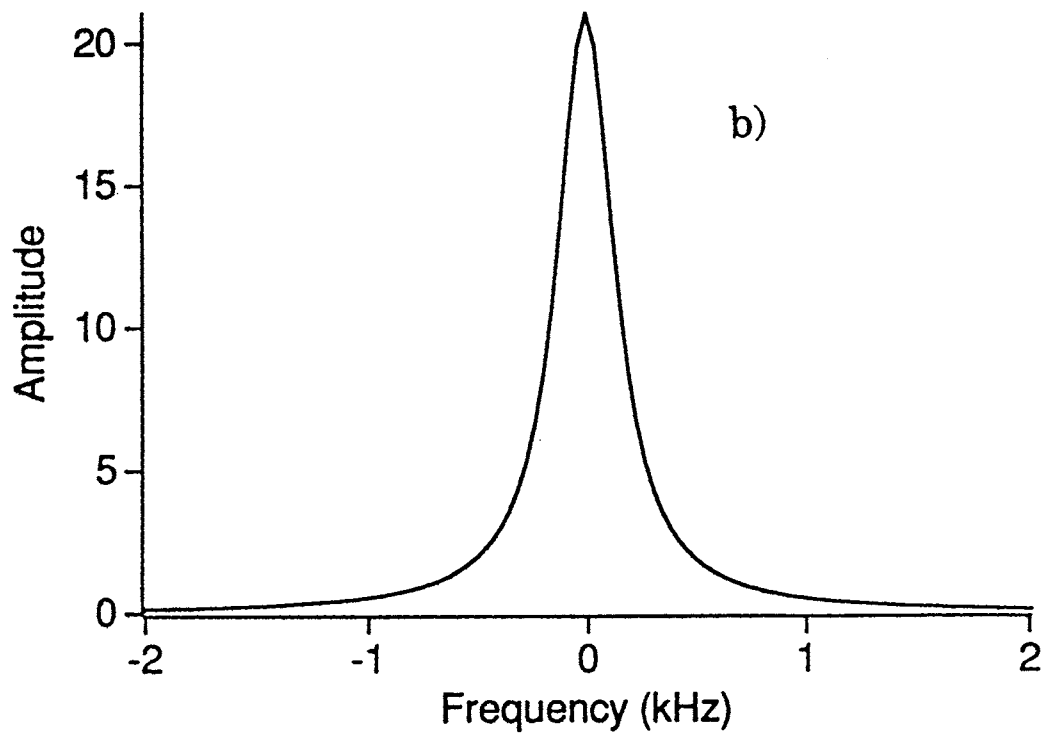
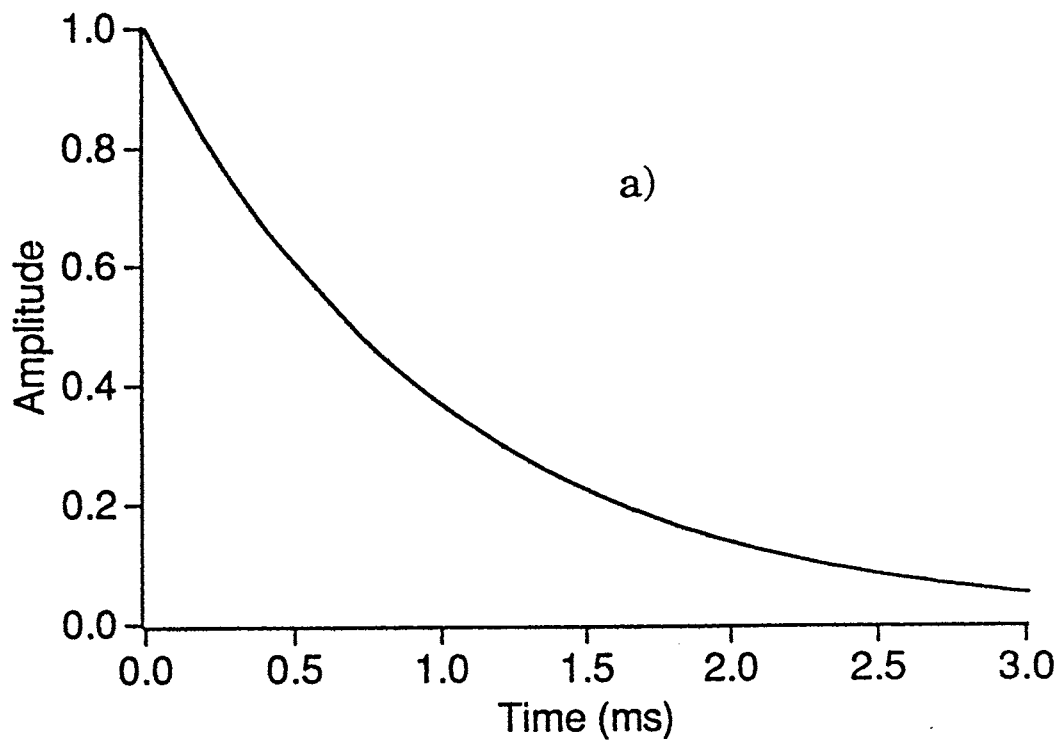


Figure 1. (a) Real part of an exponential time-domain, free induction decay (FID). (b) Real part of the Lorentzian spectral distribution which is the Fourier transform of the curve shown in (a).

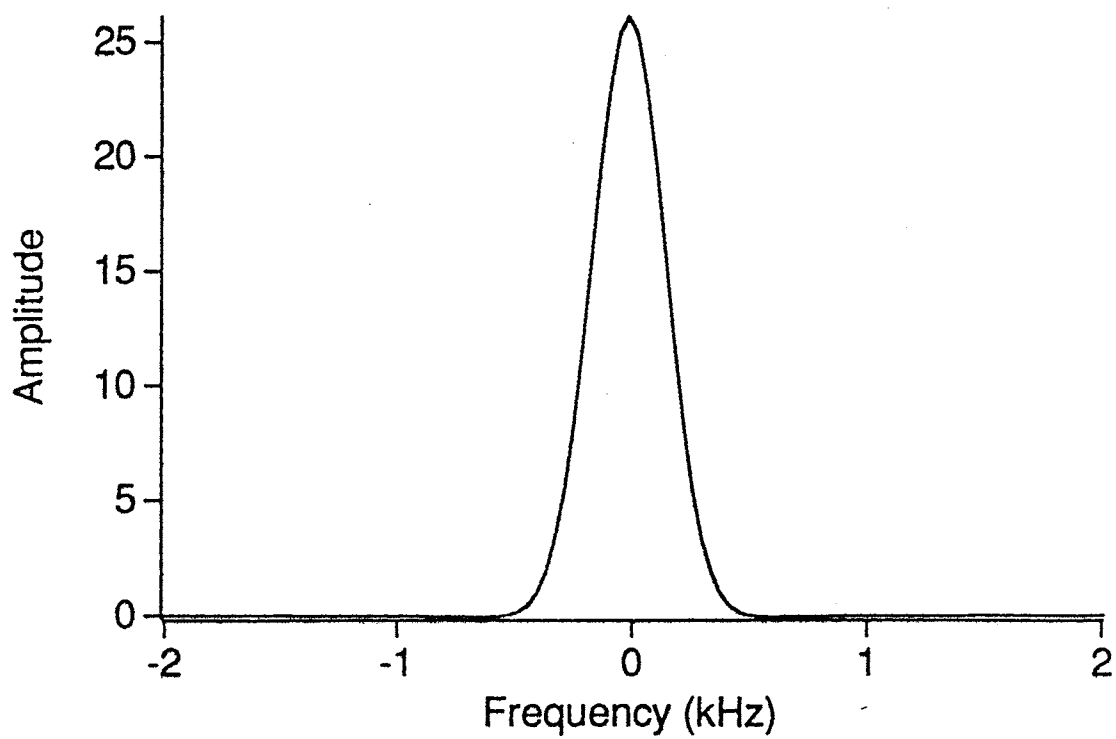
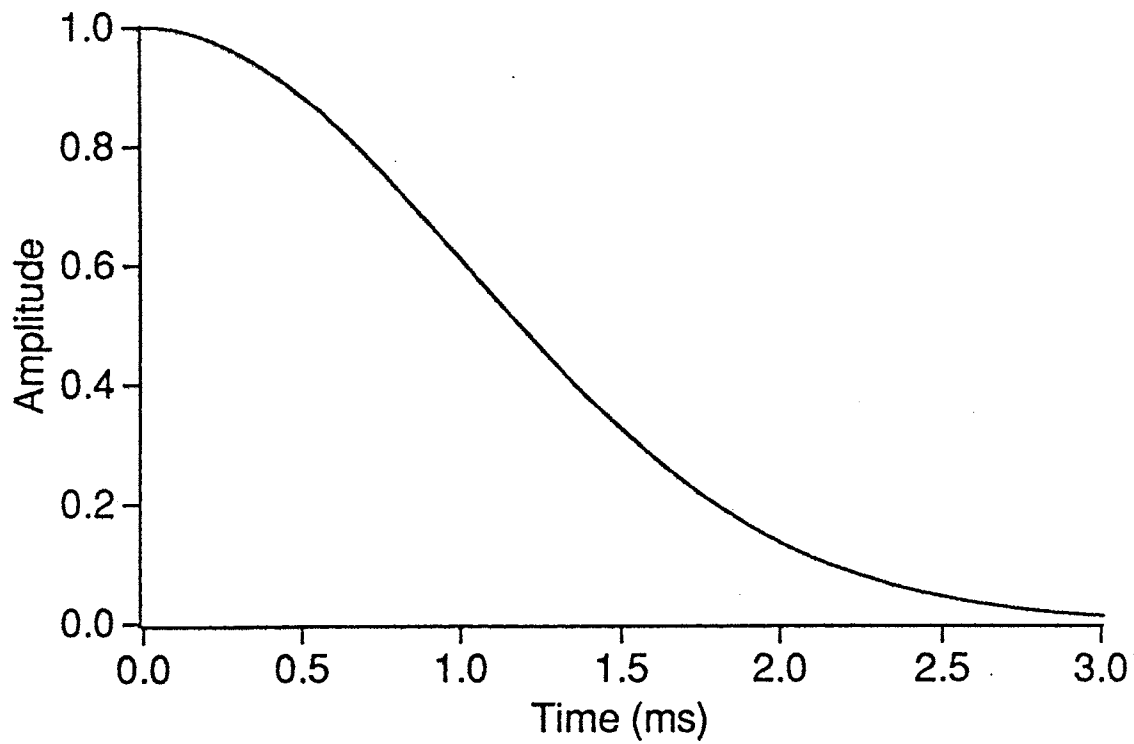


Figure 2. (a) Real part of a Gaussian time-domain FID. (b) Real part of the Gaussian spectral distribution which is the Fourier transform of the curve shown in (a).

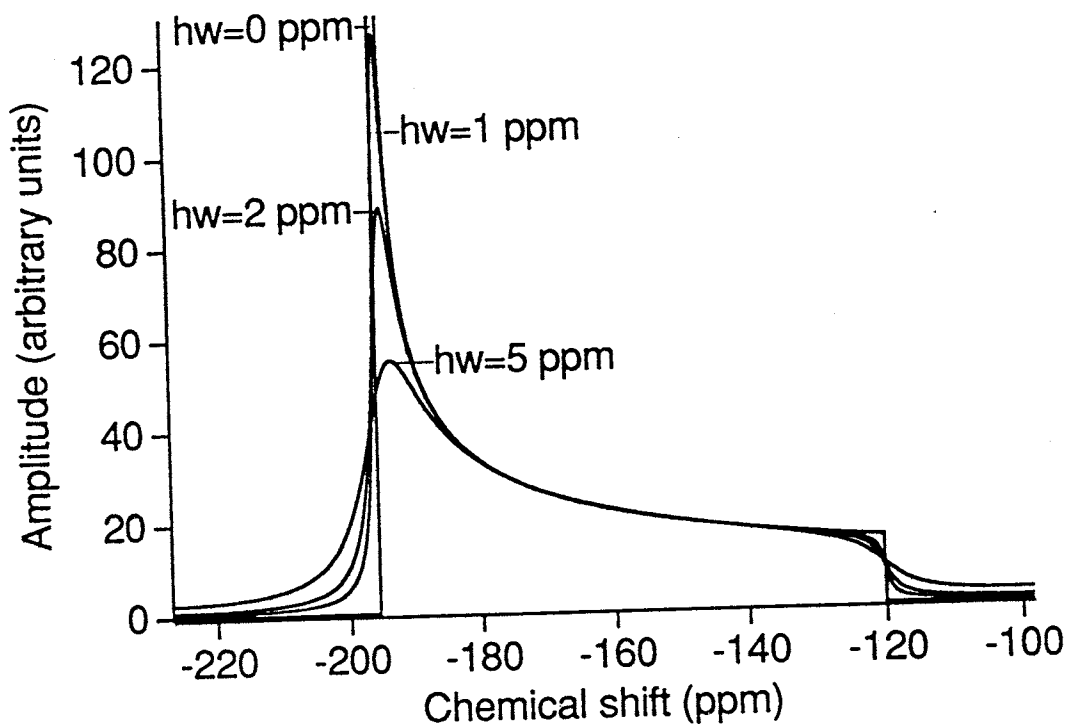


Figure 3. ^{13}C powder patterns typically found in carbonates. Different curves correspond to different amounts of spectral broadening which is indicated by the half-width (hw) label on each curve. (See text for derivation of curves.)

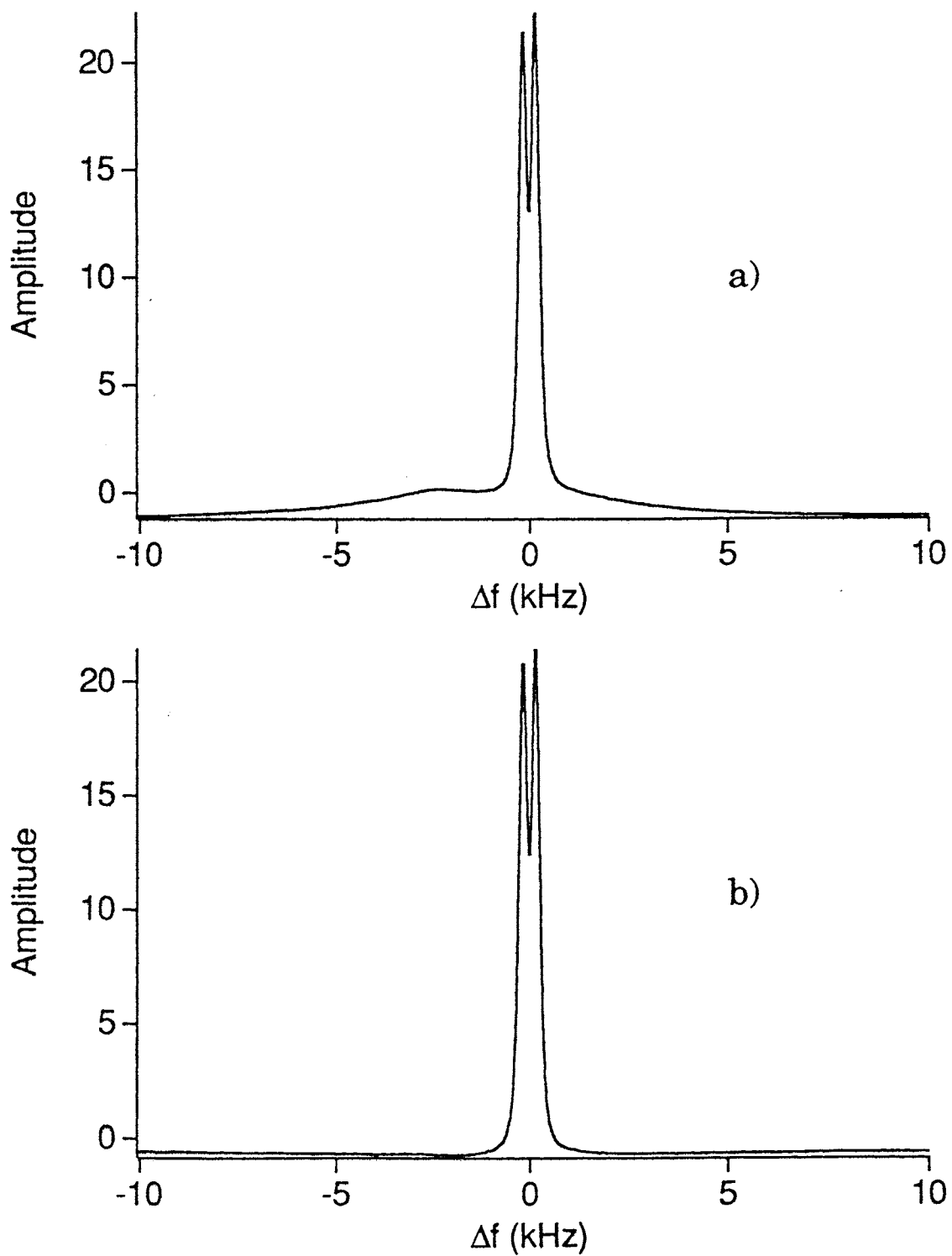


Figure 4. (a) Proton spectrum for Bentheim sandstone containing water and Soltrol-130 as described in Table 1, second pass.. Note broad baseline bump. (b) Spectrum after background subtraction corrections applied to spectrum shown in (a).

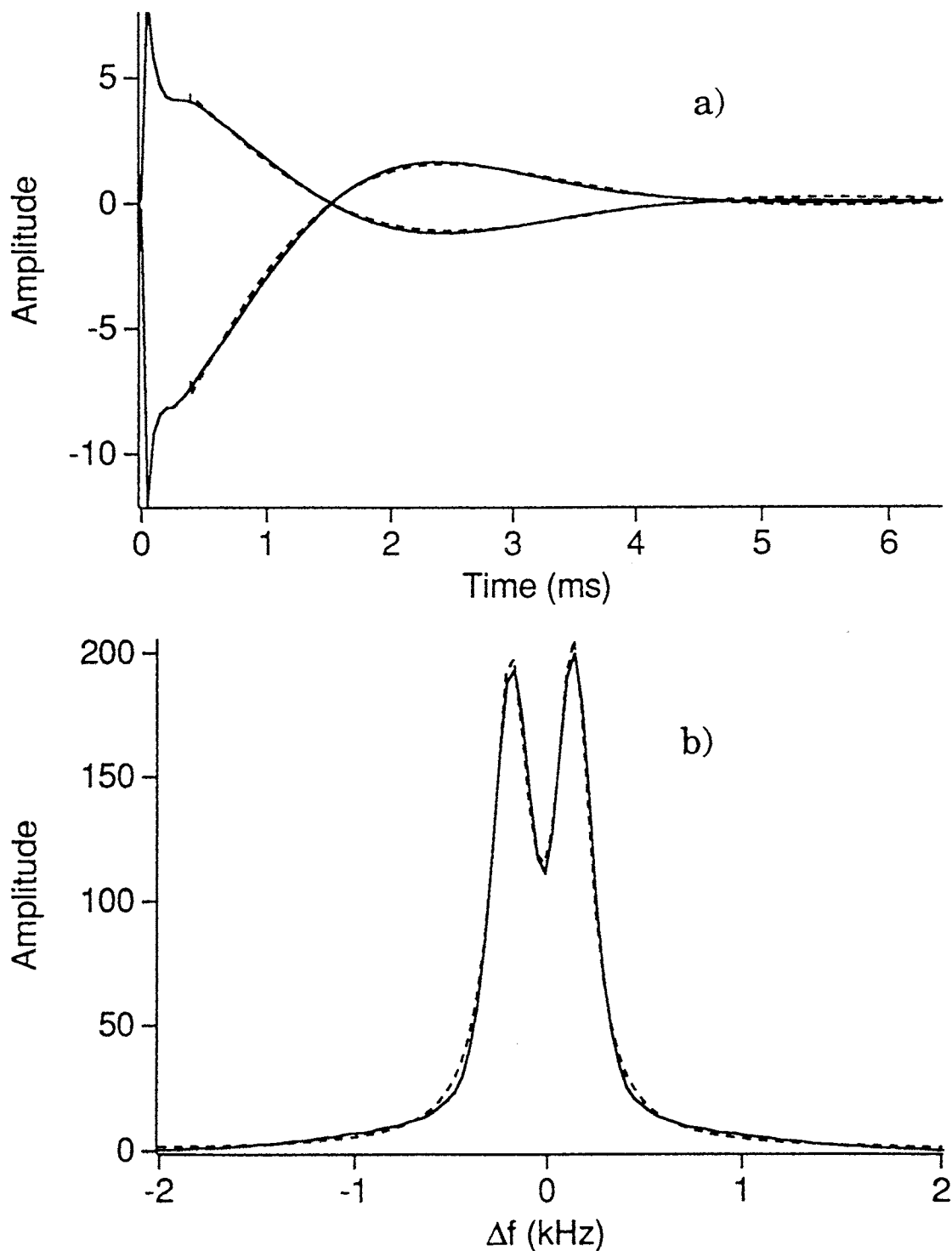


Figure 5. Proton NMR for water and Soltrol-130 in Bentheim sandstone as described in Table 1, second pass. a) Real and imaginary parts of the time-domain FID (solid lines) with theoretical fit (dashed lines). b) Experimental (solid line) and theoretical (dashed line) spectra. Note that the first several points of the FID were left out of the fit. The kink at the beginning of the data corresponds to the broad background hump shown in Fig. 4(a).

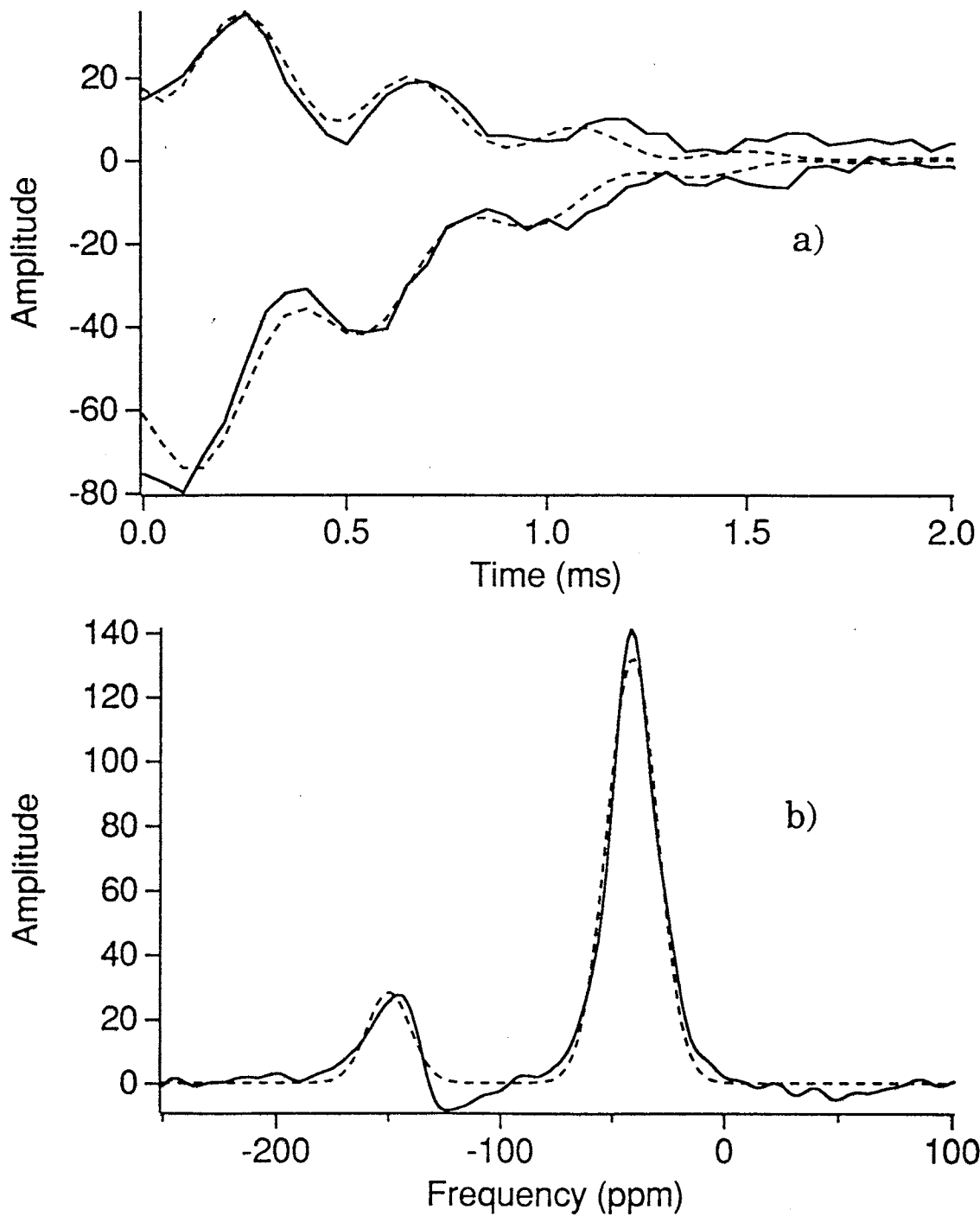


Figure 6. Wasson crude oil in Bentheim sandstone. a) Real and imaginary parts of the time-domain FID (solid lines) with theoretical fit (dashed lines). b) Experimental (solid line) and theoretical (dashed line) spectra. The experimental spectrum is made by adding some theoretical points to the measured FID to replace lost initial points.

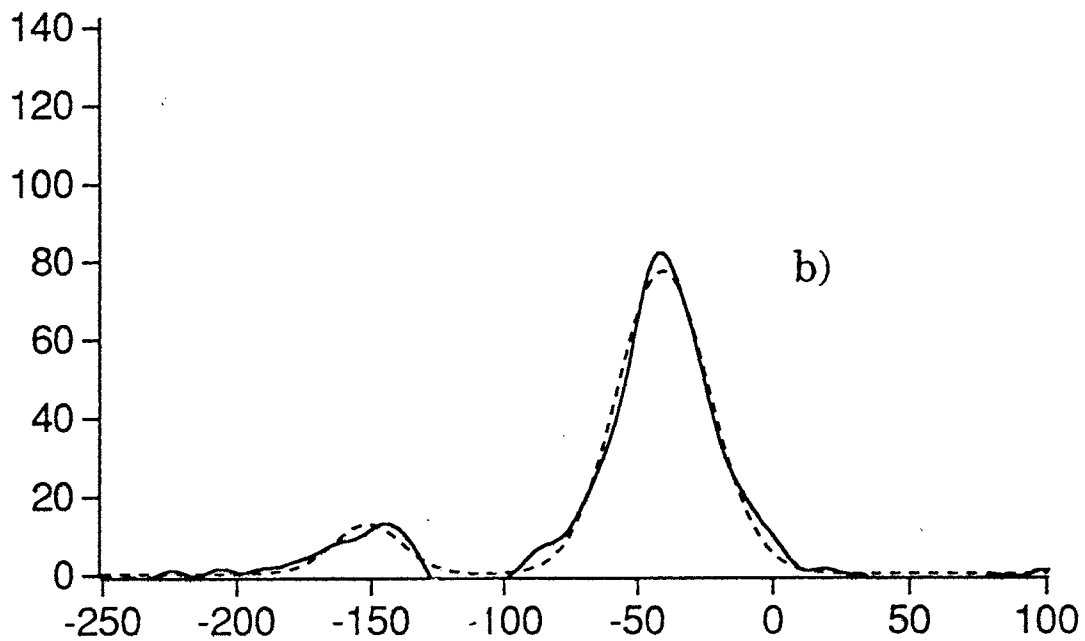
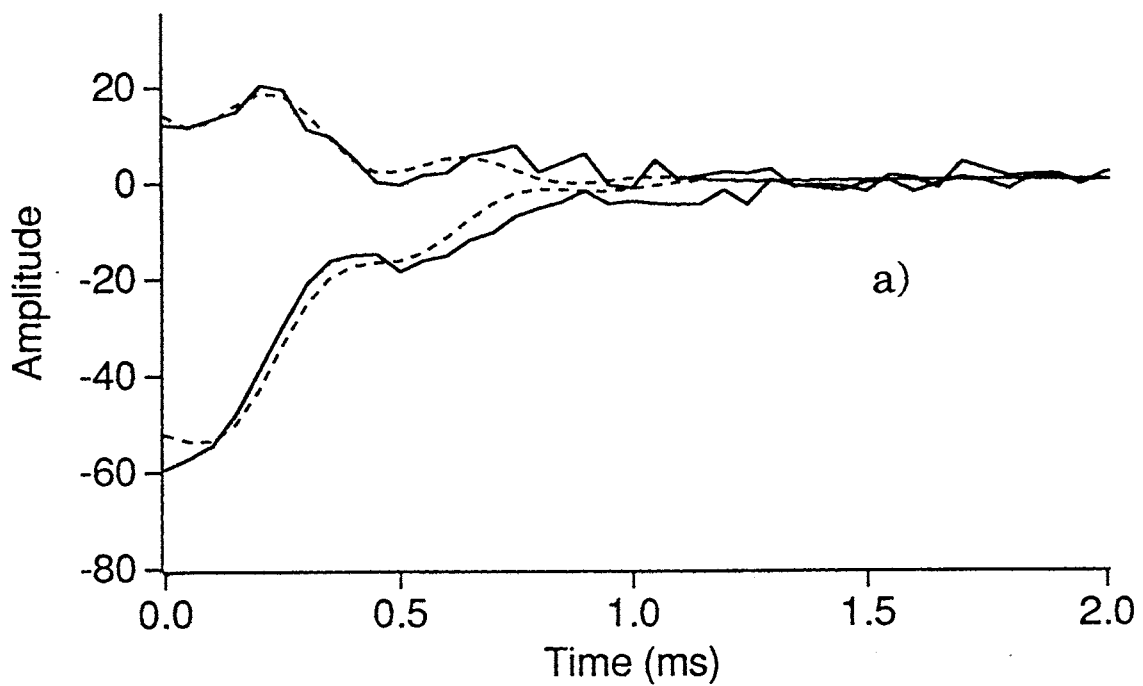


Figure 7. Wasson crude oil in Berea sandstone. a) Real and imaginary parts of the time-domain FID (solid line) with theoretical fit (dashed line). b) Experimental (solid line) and theoretical (dashed line) spectra. The experimental spectrum is made by adding some theoretical points to the measured FID to replace lost initial points.

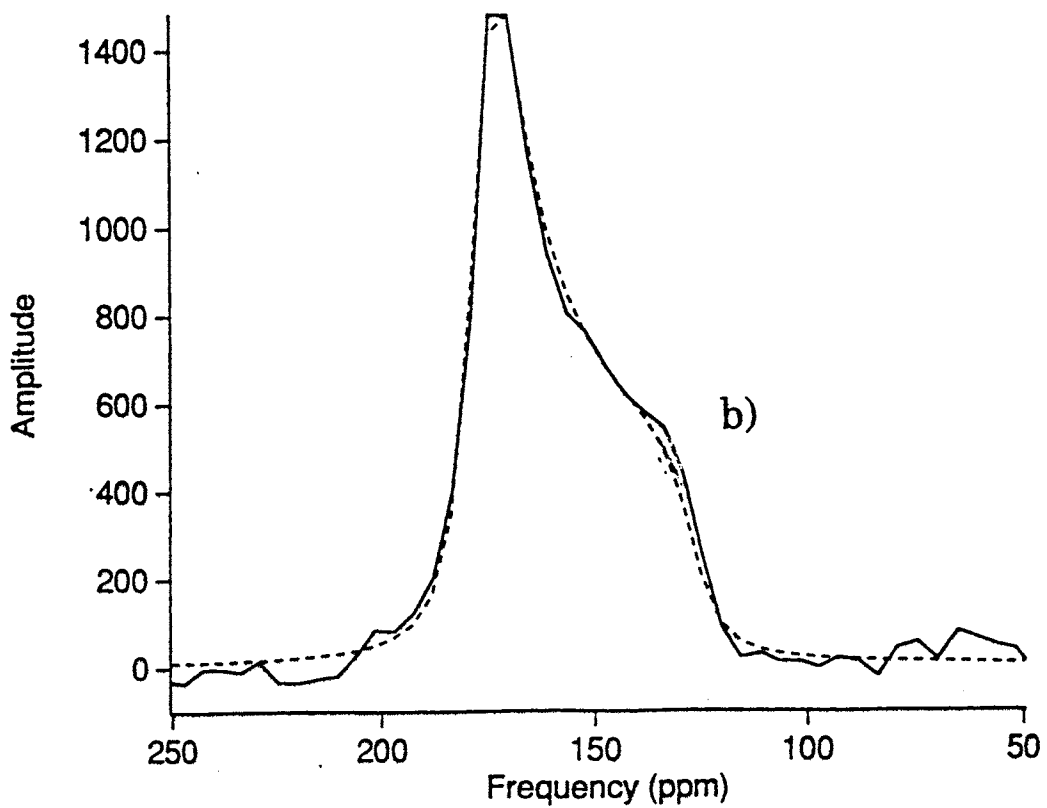
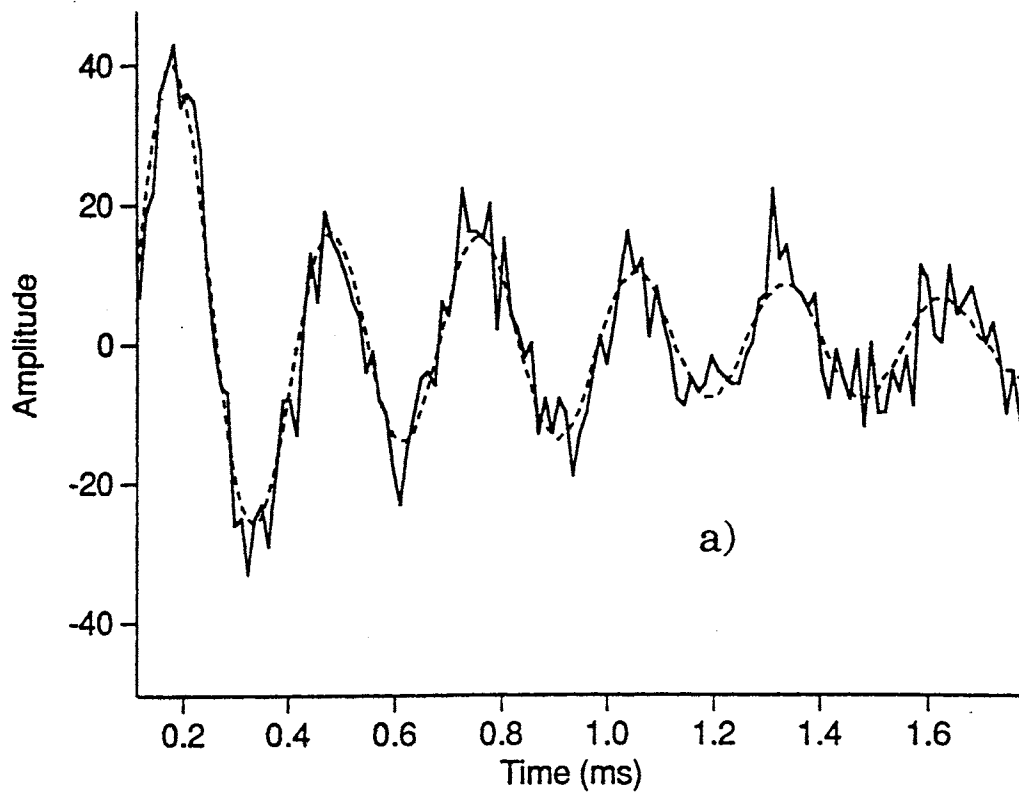


Figure 8. Carbonate in Indiana limestone. a) Time-domain fit to one quadrature component of FID. b) FT of empirical data and theoretical fit.

